

HYDROGEN TRANSFER DURING DIRECT COAL LIQUEFACTION WITHOUT HYDROGEN OVERPRESSURE

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INTRODUCTION

Since the late 1960s, the British Coal Corp. has been concerned with the development of two coal liquefaction processes, both of which depend upon a liquid solvent at low pressure to extract the coal. The first of these was designed to extract a precursor suitable for the manufacture of electrode coke (1). In the second process, the extraction step was modified by the introduction of hydrogen donors into the solvent and employed as the first stage of a two-stage liquefaction process (Liquid Solvent Extraction, LSE) whose net products were distillate transportation fuels(2). Pilot plants of about a ton per day for each process have been built and operated successfully.

This paper is primarily concerned with the LSE process and will consider the significance and effects of solvent hydrogen transfer on the performance and operation of the first stage, its influence on subsequent process steps, and on the overall process.

LSE PROCESS DESCRIPTION - A schematic of the process is shown in Fig. 1

Coal is dried, pulverised and slurried with a hydrogen donor recycle solvent. This solvent, which is a mixture of aromatic and hydroaromatic hydrocarbons is produced within the process and is entirely coal-derived.

The coal slurry is pressurised to 20 bar, preheated to the reaction temperature of 410°C and fed to a digester in which up to 95% of the coal is dissolved. The use of elevated pressure in this stage is to prevent undue vapourisation of the solvent. During the digestion process, hydrogen is donated from the solvent to the coal structure as it breaks up, stabilizing the lower molecular weight fragments and preventing retrograde reactions. The resulting digest contains dissolved coal ('extract'), residual coal solids and the mineral matter originally present in the coal.

The digest is cooled to 300°C, reduced in pressure and filtered to remove the mineral matter and the undissolved coal. The filtrate, which is solids free and has a very low ash content (i.e. less than 0.1%), is known as 'coal extract solution'. The filter cake is washed with a low boiling fraction of the solvent, which displaces the coal extract solution trapped within the voidage of the cake. Residual wash oil is in turn recovered by vacuum drying the filter cake. This washing and drying procedure minimises the loss of extract and solvent with the cake.

In the second stage, the coal extract solution is pressurised, typically to 210 bar, mixed with hydrogen gas, preheated and fed to ebullated bed hydrocracking reactors. These reactors operate at temperatures in the range 400 - 450°C. Standard oil industry heavy residuum hydrosulphurisation catalysts can be used.

The product from hydrocracking is distilled to recover the recycle solvent (boiling above 300°C) and to give three main products: LPG, naphtha (boiling below 180°C) and mid-distillate (boiling range 180-300°C). In addition, a by-product pitch stream (nominally boiling above 500°C) is taken off, although most of the material in this boiling range is recycled as part of the solvent. The remaining by-product streams contain light hydrocarbon gases, predominantly methane and ethane, and heterogases. An appreciable proportion of the oxygen originally present in the coal is emitted as CO₂, reducing the overall hydrogen consumption.

In addition to the process configuration described above, several alternative processing options have been examined which may be appropriate under some economic conditions. The pitch by-product may be fed to a delayed coker to recover additional distillate and to produce a premium grade coke which is an excellent starting material for the preparation of graphites and carbon electrodes. The rehydrogenation of the recycle solvent to replace the hydrogen donated to the coal during digestion may be carried out in a separate reactor on a fraction of the solvent recovered by distillation from the filtrate. Finally, if saturated hydrocarbon (which are not hydrogen donors) build up in the solvent, a portion of the solvent may be fed to a 'satcracker' in which the saturated compounds are thermally cracked to lower boiling liquids and gases.

The main features of the LSE press which distinguish it from other two-stage direct liquefaction processes are therefore the low pressure first stage and the removal of solids by filtration, both of which reduce capital costs. All coals except anthracites can be processed, although some energy penalties are associated with the use of lignites.

Over the past 25 years the British Coal team of workers have built up expertise in the various unit operations, based partly on practical plant experience and partly on more fundamental laboratory studies, mainly but not solely with bituminous coals.

Although it became apparent that each stage of the process affected the others, this paper will now concentrate on the dissolving (or extraction) stage and in particular upon hydrogen transfer and retrogressive reactions therein.

The aim of most current coal liquefaction processes is to produce distillate fuels in high yield and thus much effort has been expended in trying to minimise retrogressive reactions which eventually lead to coke formation. In contrast in the Electrode-coke process (Fig. 2) maximising the quantity and quality of extract derived coke was the aim; it is thus relevant to review some of the studies of this process to assist understanding of retrogressive reactions.

DIGEST VISCOSITY

Studies of the changes in slurry viscosity during extraction process have shown that, regardless of temperature and solvent to coal ratio, the same general time-dependent pattern was observed(3) for bituminous coals, Fig. 3.

Starting from the slurry (A) there is an initial rise in viscosity (Zone B) which takes place rapidly at all temperatures studied, reaching a peak within a few minutes, possibly within seconds. The peak viscosity in this region is at least five times that of the untreated slurry. Comparison between the physical state of a slurry which consists of 20-25% rigid particles in a fluid (anthracene oil), with that of a digest of large polymers, formed from the dissolving coal, and intimately dispersed within the same fluid, enables the change in viscosity during digestion to be appreciated. It is also known that the coal particles themselves swell prior to their disintegration and this phenomenon too is thought to contribute to the viscosity increase.

After reaching a peak the digest viscosity drops continuously over a period of about 20-30 mins., (Zone C) a time found to be independent of temperature. However, the minimum viscosity reached at the end of this zone was temperature dependent, the higher the temperature the lower the viscosity. This result indicates more extensive depolymerisation at higher digestion temperatures. Furthermore, the initial rate of viscosity reduction was found to increase markedly with increasing temperature. At the lower temperatures studied, the rates of change of viscosity over the same viscosity range can be compared reasonably accurately. The time taken for the viscosity to decrease from 2.5 to 1.5 cP (measured at 250°C) was 20 mins. at 380°C and 5 mins. at 400°C. From these data, an activation energy of 60 kcal/g mole can be calculated, indicative of a process involving the breaking of moderately strong chemical bonds. It was considered that the kinetics observed were the result of the combination of several reactions; however, the cause of the reduction of viscosity is attributed solely to the depolymerisation (i.e. reduction in molecular weight) of the coal extract.

After about an hour (total time) the viscosity then begins to increase again, independently of temperature (Zone D). The polymerisation reactions occurring in this zone which cause the second viscosity increase obviously started before the end of depolymerisation stage and it is the combination of these two reactions that controls the position of the minimum at the end of Zone C. The rate of increase of viscosity is not greatly enhanced between 380 and 420°C indicating a low activation energy for this process which is consistent with polymerisation reactions.

Finally, the reduction in viscosity during Zone E is explained as due to the growth of mesophase in which the higher molecular weight coal extract components are concentrated into many small areas within the remaining fluid which is of lower viscosity, hence creating a relatively dilute continuous phase. The end of zone E represents a slurry of coal extract mesophase in solvent.

It was also realised that beyond Zone E and under exceptionally severe conditions, the whole digest, including solvent, would coke and thus the viscosity would rise again; this is definitely a zone that there is every incentive to avoid in any process!

Assessments of coke properties confirmed that by employing digestion times much longer than those necessary for extraction there was some improvement in final coke quality, presumably because the mesophase liquid crystals had been given time to grow before coking became too advanced. Such a step is now known to be essential to the formation of graphitisable carbons.

The quinoline insolubility of the slurry or digest shows an initial reduction (Zone B & C) as the coal is taken into solution. It then rises in a manner consistent with a 2nd order, polymerisation reaction, i.e. more rapidly as the solvent to coal ratio is reduced.

Several lessons and questions which are relevant to coal liquefaction in general emerge from these studies of the electrode coke process.

(1) to minimise retrogressive reactions then, all other things being equal, a high solvent to coal ratio should be used. In process development there are often strong pressures from design and costing engineers to reduce the amount of recycling solvent which has to be handled for a given coal throughout. Those applying these pressures rarely take into account that small improvements in the overall conversion to liquid products could be more valuable than the cost of increasing the solvent to coal ratio substantially; this is particularly so if the solvent doesn't all have to be distilled.

(2) similarly, as soon as extract is taken into solution it should be diluted with the other liquid phase (i.e. solvent). Presumably small particle size would help in this respect as would agitation that resulted in high particle Reynolds numbers.

(3) if conditions that produce some coking occur somewhere in the process after extraction (e.g. in preheaters or on catalyst surfaces) then is it better to allow those species that polymerise more rapidly to do so in the extraction stage, as they will be removed along with the residual coal (e.g. in the subsequent solid-liquid separation step-by filtration in the LSE process), thereby increasing the life of catalyst and preheater.

(4) what is the relative ease of hydrogenation and hydrocracking of molecules that are truly in solution compared with the same species arranged in mesophase liquid crystals? In other words is the irreversible point in inevitable coke formation at the liquid crystal ordering stage or after further polymerisation?

(5) the presence of hydrogen, either as H_2 or in hydrogen donor solvents, is well known to reduce the rate of carbon (strictly it is still only a semi-coke) deposition on catalysts and to dramatically reduce viscosity. This does not mean however that hydrogenated extract doesn't polymerise or form mesophase. Indeed given suitable conditions, bigger and better liquid crystals can be formed resulting in excellent needlecoke because the hydrogenation reactions help to remove some of the heteratoms thereby reducing the steric hindrance to perfect alignment of aromatic layers. This is desirable if coke is aimed to be the end product but the formation of micron-sized mesophase spheres in the digester, perhaps due to imperfect mixing or just exhaustion of hydrogen donors in the solvent, could cause problems in the solids separation stage due to their plastic deformable nature.

LIQUEFACTION AND H-TRANSFER

The term coal conversion is used with different meanings and can cause confusion. It can mean the extent of conversion into liquid and gas, a secondary solvent, quinoline, cresol or THF, being used to determine the insoluble organic matter (IOM). In other cases conversion is defined as the yield of liquids boiling below say 450°C.

It is reasonably well accepted that little coal will dissolve in most solvents below 200°C (although work with NMP with and without CS_2 can give extensive solution of some coals (4)). However at the temperature of most liquefaction processes, i.e. around 400°C, the majority of most coals (except anthracite) can be taken into solution. Using phenanthrene or recycled anthracene oil without hydrogen over pressure, up to 80% of bituminous coal appears in the filtrate. Much of the extract can be insoluble in THF and some, even insoluble in quinoline which implies molecular weights in excess of 2000.

Is this conversion? One could say that the coal has merely been reconstituted without its mineral matter and some of its macerals, e.g. the inertinite. To support this is the fact that the softening point of such pure extracts is over 300°C, i.e. only a little lower than of the coal; it takes the addition of about 2% hydrogen to reduce the extract softening point to around 150°C (e.g. as in the SRCI process or as has been observed when using tetralin as solvent(7)).

The amount of coal taken into solution is enhanced by the presence of hydrogen, either from a donor solvent or as gas. The molecular weight of the extract is reduced as has just been mentioned, but whether this is instantaneous or caused by a sequential reaction is open to discussion. Is it that the extra taken into solution when donor hydrogen is available is due to the avoidance of very rapid retrogressive reactions by some thermally produced radicals, as is perhaps suggested by recent work, (5), or is it that the hydrogen is contributing directly to the dissolution reaction?

Whatever the reason, there is no doubt that more coal appears in solution when hydrogen donors are available, and that for a given coal the extra conversion is dependent on the amount of hydrogen transferred. Thus it seems reasonable to assume, for the purposes of process development and reactor design, that until proven otherwise, there are two discrete steps i.e. coal solution and liquid

phase hydrocracking of the coal extract. In some process designs it all happens in a single reactor whereas in LSE for example the first reactor is primarily for dissolution and the second reactor for hydrocracking. Specific conditions can be chosen for each reactor, rather than the necessary compromise when a single reactor system is used.

COAL EXTRACT QUALITY

Increasing extraction to the maximum possible extent would be desirable if all the coal molecules taken into solution were identical. But bearing in mind the variation of the hydrogen contents of the macerals that make up the bulk coal (e.g. 7% in liptinite to under 4% in some of the so-called "inertinite" that can be dissolved) this is unlikely to be even an approximation of the truth. In deciding whether maximum extraction is the optimum the most important properties of the coal extract molecules are their rate of hydrocracking and the consequent yield of desired product (i.e. gasoline rather than gas), and the hydrogen consumption needed to achieve this. Whilst experimental measurements of the amount of coal going into solution can be quickly and accurately determined experimentally the same cannot be said for the hydrocracking properties just mentioned.

In studies (6) of the reactivities of coal extract solutions, samples were made from different coal preparation plant streams, in which both mineral matter and maceral distribution varied. Although extents of dissolution varied with inertinite content by as much as 10% differences in hydrocracking could not be distinguished because of experimental reproducibility. These coal samples were far from pure macerals so it cannot be concluded yet that there aren't differences between maceral extracts from the same coal. All other things being equal, which is rarely the case in coal science, one would consider it desirable to have a high liptinite content in the feed coal because of its high hydrogen content. Unfortunately a lot of this hydrogen is in alkyl groups and probably results in higher yields of less valuable gaseous products.

Overall it should be mentioned that advantage could be taken of modern dense media coal cleaning technology in a commercial liquefaction plant with the clean fraction going to liquefaction and the middlings fraction to utilities. As shifts of small amounts in the extent of conversion (whether it be to extract or to finished products) have very significant effects on plant economics, it is still desirable to do further work quantifying the magnitude of any difference between maceral extracts.

SOLVENT QUALITY

In any plant the solvent has to be recycled and thus although useful studies can be performed using pure compounds and doing once-through i.e. single cycle, experiments, eventually recycle must be studied. Whilst the biggest change takes place over the first recycle, changes can continue for a long time as the solvent becomes truly process-derived. Monitoring and then controlling these changes can present a big challenge.

In experimental work a 102% solvent mass recovery should be aimed for to allow for overall losses that are likely to occur even with the most rigorous housekeeping. If there is a slight solvent surplus then it can be converted into lighter products without much effect on plant economics; if there is a solvent deficit the process isn't viable.

In most liquefaction processes, including LSE, the process solvent consists of material boiling above 300°C and includes some above 500°C (which is extract that is not 'converted' during hydrocracking). From studies with various pure compounds and process solvents particularly hydrogenated phenanthrenes and pyrenes, it has been concluded that di- and tetra hydro-derivatives are the most reactive and that they are preferred to the extensively hydrogenated species (i.e. the hexa or octa hydro-derivatives). It is thus preferable to have every molecule hydrogenated to a small extent rather than a few heavily hydrogenated species. As the maximum amount of hydrogen transferred to the coal during extraction is only 1 - 2% of coal, this represents less than 1% on a solvent basis (equivalent to that which can be provided by di-hydro species of aromatics boiling between 300°C and 500°C). The levels of hydrogen donors should of course be above the minimum so that even at the end of the digestion stage there is still a concentration of hydrogen donors available to cap further radicals that are formed by continuing albeit slower thermal cracking of coal and extract molecules.

Not all the hydrogen donated by the solvent reaches the desired recipient, i.e. the extract. About a tenth ends up as molecular hydrogen and represents an inefficiency. If catalyst is present it merely enhances solvent dehydrogenation and thus increases the yields of IOM and hydrogen. The hope that catalyst might enable hydrogen to be released from the solvent at an appropriate rate to match coal radical formation has not been realised. This is perhaps yet another indication of the difficulty of having coal, hydrogen and catalyst and maybe solvent simultaneously present at the same reaction site.

MONITORING RECYCLE SOLVENT

While proton NMR has proved extremely useful for monitoring short term changes during dehydrogenation (i.e. extraction) and rehydrogenation it is, however, not so good for estimating absolute concentrations of hydroaromatics. Generally, the use of NMR is limited for tracking if there is the possibility of slow long term changes in the solvent composition. In plant operations another reason to aim for 102% solvent recovery is as a way of limiting the build up of undesirable trace species in the solvent.

It is also necessary to have a method of determining if the extracting power of the solvent is decreasing *before* the point is reached when plant filter cake yields rise and other operational problems due to insufficient hydrogen transfer set in. Remedial action, e.g. by increasing hydrogenation or sat-cracking, would then have a chance of recovering the situation.

Early in the LSE project this need was especially pressing in convincing a potential sponsor that the LSE process could cope with their lignite and the author promised to devise such a test in time for the recycle run due to take place a few months later. So was born SDI, or Solvent Dissolving Index to give it its full name.

The test (7) involves diluting by a known amount a sample of the solvent with a non-hydrogen donor (usually, but not necessarily, naphthalene) so that there are less hydrogen donors than required to ensure maximum extraction when a mini-bomb test is done with this diluted process solvent.

Tests for the particular coals in use with well characterised solvents enable calibration graphs to be constructed Fig. 4 & 5 in which nominally an SDI of 10 means that there are just enough hydrogen donors to ensure maximal extraction

In practice it was found that a certain margin above this minimum was desirable, i.e. 3 or 4 but the SDI fulfilled its major objective of enabling the changes in recycle solvent donor properties to be confidently monitored. As with testing coals the best test of a solvent is to perform an actual extraction.

Non distillate fractions of recycle solvents (i.e. pitch) were shown to be excellent solvents, those with softening points under 200°C having SDI's greater than 10. Such pitches have little hydrogen donor ability and contain plenty of coke precursors so that when used alone extractions reduce if severe digestion conditions are used (i.e. above 420°C). However, as they are normally diluted with distillate material this is rarely a problem and keeping a certain level of pitch in the recycling solvent became generally regarded as advantageous, helping to keep everything in solution, being intermediate in MW etc between solvent and extract, but compatible with both.

At almost the opposite extreme are the light end saturates which are basically not hydrogen donors. The alkanes which usually represent about a quarter of these are thought to be formed directly from the coal. For Point of Ayr coal this is about 0.3% coal (8) whereas for the lignites it can be much greater. The others, i.e. naphthenes, are formed in the hydrotreatment stage and once formed are difficult to dehydrogenate, as was found in many attempts to achieve this catalytically. It was found, however, that if only aromatics and naphthenes were present then the naphthenes did donate some hydrogen and extraction levels above that expected from the pure aromatics were achieved (9). However, hydroaromatics donate their hydrogen first and the naphthenes later, if at all. Various ways of trying to utilise this interesting effect were considered but none proved practical.

CONCLUSION

In order to achieve maximal coal extractions and to minimise retrogressive reactions of the extract, the recycle solvent must be in adequate supply and of the right properties, i.e. good hydrogen donor ability as well as good physical solvent properties.

It is noteworthy that during the 70's and 80's other liquefaction process developers, who without exception used high pressure hydrogen during extraction, gradually came round to the view that having a 'good' solvent present made their processes work better, i.e. "hydrogen donor species could reach places that ordinary (gaseous) hydrogen could not".

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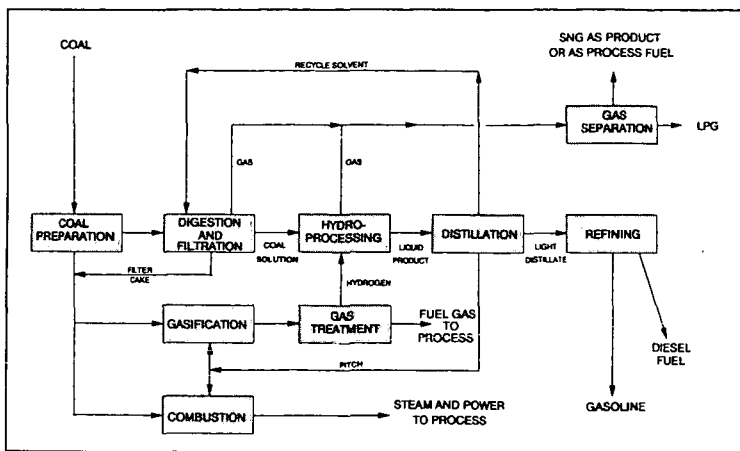


Figure 1 The Liquid Solvent Extraction Process

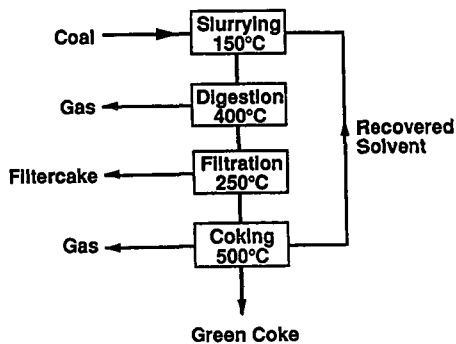


Figure 2. Electrode Coke Process

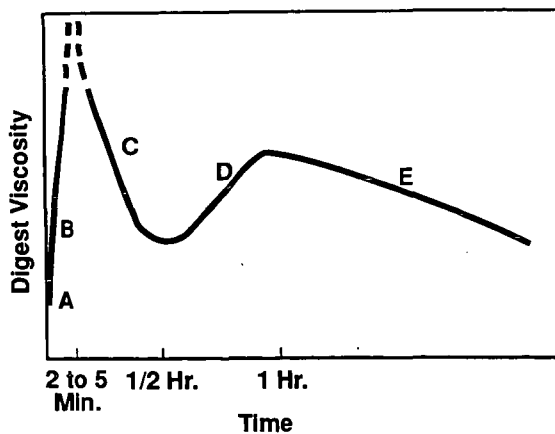


Figure 3. Effect of Digestion Time on Viscosity

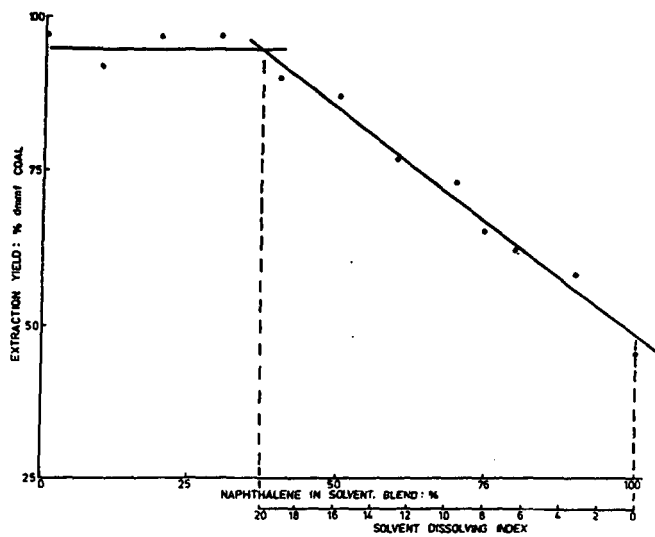


FIGURE 4. SDI CALIBRATION FOR THE LIGNITE

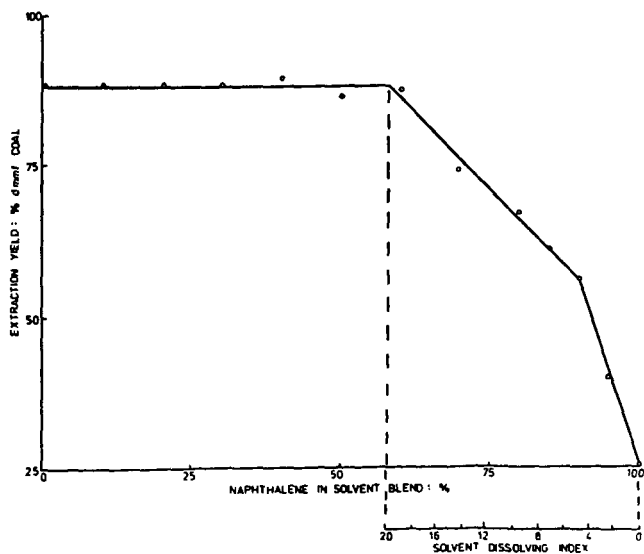


FIGURE 5. SDI CALIBRATION FOR THE BITUMINOUS COAL